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METHODS FOR DETERMINING PELLET VOLUMES AND EFFECT ON FREE SWELLING INDICES

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METHODS FOR DETERMING PELLET VOLUMES AND EFFECT ON FREE SWELLING INDICES

by

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ABSTRACT

Free Swelling tests were done on three pellet types according to the proposed procedure stated in ISO TC 102/SC3N605. The pellets were examined by measuring their volumes before and after reduction in order to evaluate several new methods being considered by ISO Technical Committee 102- Subcommittee 3 as alternatives to the mercury displacement method. Other volumetric methods studied included: linear, buoyancy in water, oleite-kerosene- Gakushin (O.KG). Results indicated that the four methods gave the same relative order for pellet swellings. Results from the OKG and the buoyancy in water methods were similar for each pellet type and much lower than results from the linear method which seems to be the least accurate. The results from the mercury displacement method were the lowest of all procedures investigated and this is attributed to the intrusion of mercury into larger pores of reduced pellets. The buoyancy in water and the OKG methods appear to be accurate. Reduced pellets oxidized after their volumes were measured using the buoyancy in water method making the method undesirable if any further analysis is required. The OKG method gave swelling indices and degrees of pellet reduction similar to the buoyancy in water method. The relative free swelling indices of the pellets tested appeared to have an inverse relationship with surface area and total pore volume of the non-reduced pellets. Swelling appeared highest for the pellets having the lowest amount of mesopore and macropore volume.

MÉTHODES POUR DÉTERMINER LE VOLUME DES GRANULES ET L'EFFET DE CELUI-CI SUR LES INDICES DE GONFLEMENT LIBRE

par

J.T. Price, J. MacDougal, R. Villeneuve et J.F. Gransden

RÉSUMÉ

Trois genres de granules ont été soumises à des essais de gonflement libre conformément à la méthode proposée par le sous-comité 3 N605 du Comité technique 102 de l'ISO. On a procédé à l'étude des granules en mesurant leur volume avant et après la réduction en vue d'évaluer plusieurs nouvelles méthodes que le Sous-comité 3 du Comité technique 102 de l'ISO se propose d'utiliser pour remplacer la méthode par déplacement du volume du mercure. Les autres méthodes volumétriques qui ont fait l'objet d'une étude comprennent la méthode linéaire, la flottabilité dans l'eau, l'oléite/kérosène de Gakushin (OKG). Les résultats indiquent que le gonflement des granules s'est produit dans le même ordre, quelle que fut la méthode utilisée. Les résultats obtenus à partir des méthodes OKG et de flottabilité dans l'eau, ont été identiques pour chaque type de granule et de beaucoup inférieurs aux résultats obtenus par la méthode linéaire qui semble la moins précise. Les résultats obtenus avec la méthode par déplacement du volume du mercure ont été les moins élevés des résultats découlant des méthodes étudiées et ceci est dû à l'intrusion du mercure dans les pores les plus larges des granules réduites. Les méthodes de flottabilité dans l'eau et OKG semblent exactes. Les granules réduites se sont oxydées après que l'on eut mesuré leur volume en utilisant la méthode de flottabilité dans l'eau, ce qui fait que cette méthode est inappropriée si des analyses plus poussées sont requises. Les indices de gonflement et les taux de réduction des granules obtenus par la méthode OKG étaient semblables à ceux obtenus avec la méthode de flottabilité dans l'eau. Les indices de gonflement libre des granules soumises à l'essai semblent être inversement proportionnels à la surface et au volume total des granules non réduites. Le gonflement des granules dont le volume en mésopores et en macropores est le moindre semble le plus élevé.

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INTRODUCTION

Swelling of iron oxide pellets during reduction is undesirable because of the accompanying degradation and loss in strength and reduced permeability of the blast furnace burden resulting in a loss of productivity. Iron oxide pellets are often tested under simulated blast furnace conditions to determine their relative free swelling index.

The current method of volume measurement used in ISO TC102 Standards is mercury displacement. Mercury is known to be a health hazard, therefore other methods of volume measurement are being proposed and tested. The linear, buoyancy in water and the Oleite - Kerosene - Gakushin (O.K.G.) methods have been proposed to replace mercury displacement at X meetings of ISO TC102/SC3.

The objectives of this study were:

1) to test and compare the three proposed methods of volume measurement with the mercury displacement method
2) to investigate the relationship between the surface area and porosity of pellets and their relative free swelling indices.

PROCEDURE

The test samples consisted of 18 pellets(-12.5 +10 mm). The three grades of pellets used in the international round robin for the softening under load test were also used in this study. The volumes of four test samples of each grade (12 test samples in all) were determined by the linear, buoyancy in water, and mercury displacement methods. The volumes of 12 additional test samples (four of each grade) were determined by means of the OKG method and again by mercury displacement. The results of the linear, buoyancy in water, and the OKG methods were compared with those from mercury displacement.

All test samples were reduced under carbon monoxide according to the procedure stated in ISO/TC102/SC3N605E. The procedure for volume measurement was repeated for the reduced pellets. Again, the results from the three methods were compared with those from mercury displacement.

Several physical properties of the fired and reduced pellets were examined including true density, bulk density, porosity and surface area.

APPARATUS AND EXPERIMENTAL METHODS

LINEAR METHOD

The apparatus for the linear method consists of a 35 cm length of angle iron and a 45 cm steel ruler. The ruler is placed on the inner surface of the angle iron, flat against one leg of the angle. The 18 pellets are placed in a row in the "V" of the angle iron so that they are in contact along their diameters. The length of the row, L, is measured and the sample volume is calculated:

$$V_s = \frac{\pi L^3}{1944} \qquad (1)$$

BUOYANCY IN WATER METHOD

The apparatus for the buoyancy in water method consists of a 2 L beaker filled with distilled water, a Mettler PC8800 electronic balance with 0.1 g sensitivity, a steel perforated basket (75 mm dia., 85 mm h) and a tray lined with paper towelling for blotting. The balance sits on a board jutting out from the counter directly above the beaker of water. A plexiglass board with a wire attached at either end can sit on the balance and allow the basket to be weighed hanging under the balance.

The sample to be tested is dried at a temperatuire of 105± 5 ^{0}C for 2 h then cooled to room temperature in a dessicator. The sample is weighed dry (W_1). The basket is submerged in the beaker of distilled water and shaken vigorously to dislodge any air bubbles. The scale is tared with the basket in the water. The pellets are then dropped into the basket. The pellets are soaked for ten min. Every three minutes the basket is agitated back and forth 3 times to aid in the release of air bubbles from the pellets. After soaking for 10 minutes, the weight of the pellets in water, W_2, is recorded and the basket is removed from the water. The pellets are placed in the tray lined with paper towelling and blotted quickly to remove any surface water. The weight of the pellets with water in their pores, W_3, is measured. The volume is calculated:

$$V_s = \frac{W_3 - W_2}{\text{density of water}} \qquad (2)$$

OKG METHOD

The apparatus for the "buoyancy in water method" is also used for the OKG method. In addition, the apparatus consists of a beaker of oleic acid solution (10^{-2} mol/l), a beaker of kerosene, and two pieces of foam rubber wrapped in gauze for blotting the pellets.

The pellets are dried for 2 h at 105 ± 5°C and cooled to room temperature in a dessicator. The pellets are placed in the steel basket and submerged in the oleic acid solution for 10 seconds. Then the pellets are dried between the two pieces of foam rubber and gauze while the steel basket is rinsed with tap water. After blotting, the pellets are placed in the steel basket and submerged in the beaker of kerosene for an additional 10 seconds. Again the pellets are blotted dry between the foam rubber and gauze while the basket is rinsed off with tap water. The weight of the test sample, W_1, is measured and recorded. The steel basket is attached to the scale and submerged in the beaker of distilled water. The basket is vigorously agitated to release any trapped air bubbles. The scale is tared and the pellets are dropped in the basket. The weight of the test sample in water, W_2, is recorded after two minutes. The volume of the test samples is calculated:

$$V_s = \frac{W_2 - W_1}{\text{density of water}} \qquad (3)$$

MERCURY DISPLACEMENT METHOD

The apparatus for the mercury displacement method consists of a piston which is made to force mercury through a basket and into a graduated glass tube. The piston can be cranked to a preset limit and can go no farther because of the stop nut. With no pellets in the apparatus, the piston is cranked to the stop nut and the mercury level, V_1, in the graduated glass tube is measured and recorded. The piston is cranked down and pellets are placed in the apparatus. The piston is again cranked up to the preset limit. The new volume, V_2, indicated by the new level of mercury in the tube is recorded. The volume of the test sample is the difference between these two volumes:

$$V_s = V_1 - V_2 \qquad (4)$$

RESULTS AND DISCUSSION

The linear method is a quick easy way to estimate the volume of a test sample of iron ore pellets. The calculations are based on the assumption that the pellets are perfectly spherical, and all the same size. Since this is not true, error is introduced into the calculation before any measurements are taken.

Pellets which swell a great amount tend to crack and perhaps fall apart. Cracked pellets or pellets with large open pores may have a "diameter" greater than that of a perfectly spherical pellet of the same volume. Thus, testing a sample of pellets by this method may result in a calculated volume larger than the true volume. A smaller than actual volume may be calculated if the pellets line up with their narrowest cross-sections in contact. It is impossible to use this method with pellets which crumble during reduction. The standard deviation results in Table I show that the linear method is the least precise method tested.

The buoyancy in water method is a simple and accurate method for measuring volumes of unreduced pellets. Reduced pellets oxidized quickly in water, thus reversing the reduction process. The reduced pellets also tended to break apart in the water, with the smaller pieces falling through the holes in the basket. After several repetitions, the test samples lost significant mass and hence volume. This loss takes the form of sediment at the bottom of the beaker.

As shown in Table I, when compared with volumes of the same unreduced test samples, the ratio of the volumes determined by buoyancy to those measured by the mercury displacement are near unity (0.997). After reduction, the ratio was also close to unity (1.04) but for each sample measured, the buoyancy in water volume was consistently larger than that of mercury displacement. This may be due to the fact that the pellets have small cracks, and larger pores after reduction. If, after blotting, the water stays in some of these cracks or pores, they will be measured (quite correctly) as part of the volume of the pellets. However, if these cracks and pores are large enough for the mercury to enter the mercury displacement method will not measure them as a volume, and therefore a smaller volume is measured. This discrepancy is seen particularly in the grade 2 pellets after reduction which have the largest percentage of macropores and mesopores (pores with a diameter of 0.0036 to 2.98 μm). From the results of the mercury porosimeter, it is seen that the intrusion volume is very low before reduction as

compared with that after reduction. This was also observed when the pellets were unloaded from the mercury displacement apparatus. The next initial volume measurement was significantly lower than the previous one indicating a loss in the mercury from the apparatus. The difference is the volume of mercury soaked up by the pellets.

The mean value of the ratios of the volumes measured by the O.K.G. method to those measured by mercury displacement is near unity (1.01) before reduction and slightly higher (1.06) after reduction. Again, after reduction every volume measured by the OKG method is larger than that of the same test sample measured by mercury displacement. With the oleic acid solution filling up the pores and small cracks, and the kerosene coating the pellets, all of the large pores and small cracks are counted as volume. But when placed in the mercury again some of the large pores and small cracks which were counted as part of the volume became filled with mercury and a small volume was measured.

These differences in volumetric measurements although relatively small for an average determination (maximum average ratio of 1.06 for pellet volume after reduction by OKG/Hg methods) when accumulated in calculating the free swelling indices can lead to considerable variations between the Hg and OKG or buoyancy methods as indicated by ΔV in Tables I and 2.

No significant differences in the relative free swelling indices (or the degree of reduction) of the samples were found between those measured by OKG and those measured by buoyancy in water. The kerosene coating in the OKG method prevents oxidation of reduced pellets in water. This is an improvement over the buoyancy in water method and perhaps the immersion time in the buoyancy in water method should be reduced.

The grade 2 pellets had the highest relative free swelling index, ΔV, with an average of 16.6 % for all methods investigated. Grade 1 pellets averaged 13.7 % swelling whereas grade 3 pellets averaged only 9.2 %.

From the results of the surface area and porosity tests on the three grades tabulated in Table 3, the amount of swelling appears to have an inverse relationship with the surface area of pellets before reduction (Fig. 1). Grade 3 pellets had the highest surface area of the three grades at 0.2256 m^2/g. These pellest swelled the least. Grade 1 pellets, which expanded more than the grade 3 pellets had a surface area of 0.0965 m^2/g.. Grade 2 pellets had a slightly higher swelling than grade 1 and a slightly lower surface area of 0.0928 m^2/g.

The pore size distribution and open porosity also appears to be related to swelling. Before reduction, grades 1 and 2 had higher percentages of micropores (diameters less than 0.0036 µm) than macropores and mesopores (0.0036-2.98 µm). Of the three grades, grade 2 had the highest percentage of micropores before reduction (96.9%). After reduction, the percentage of micropores decreased to an average of 30.7% and the amount of macropores and mesopores increased from 3.2% before reduction to an average of 56.8% after reduction. The volume percent open porosity increased from 22.8 % before reduction to an average of 49.1 % after reduction. The drastic rise in the porosity and particularly in the amount of macropores and mesopores accounts for the 17.0 % increase in volume of these pellets.

Before reduction, 84.4 percent of the total pore volume of grade 1 pellets were micro pores. As with the grade 2 pellets, after reduction, the percentage of micro pores dropped on an average to 45.4 percent and the percentage of macropores and mesopores increased accordingly. The volume per cent open porosity rose from 23.3 to 50.1% on average. This represents a 26.8% increase in porosity about the same as found for the grade 2 pellet.

Unlike grades 1 and 2, grade 3 pellets had less micro pores than macropores and mesopores before reduction. Only 56.3% of the total pore volume was micropores. After reduction, the pores size distribution had changed only slightly. The volume per cent open porosity of grade 3 after reduction increased less than for pellet grades 1 and 2 from 33.1 to 46.8%. Because a smaller amount of the total pore volume is macropores and mesopores, and there is a smaller rise in porosity than grades 1 and 2, the pellets swell less and experience less degradation.

Although pellets were not tested for strength either before or after reduction, grade 3 pellets appeared to be stronger after reduction since they always remained intact while pellets of grades 1 and 2 tended to crack and crumble after reduction.

PROBLEMS ASSOCIATED WITH METHODS OF MEASURING PELLET VOLUMES

The balance used in the OKG and buoyancy in water methods had a large top area and was susceptible to drafts making precise measurements difficult. Balance sensitivity should be at least 0.01 g. Three individual baskets should be used in the O.K.G. method, one each for soaking the pellets in liquid. By using only one basket, the kerosene became contaminated with water and oleic acid solution, and the distilled water became contaminated with tap water, kerosene and oleic acid solution. Some of the contaminants came from the pellets but most came from the basket. These contaminants changed the density of the distilled water, and introduced error into the calculation.

Care must be taken to ensure that all air bubbles are removed from the basket before taring the scale. If air bubbles remain on the basket when the pellets are dropped in some off during the soaking period the weight of the pellets in water will appear heavier than the actual weight.

Difficulties were encountered with the mercury displacement apparatus. Air bubbles in the mercury caused the volume measurement to be higher than the true value. The apparatus was vibrated in an attempt to get rid of all air bubbles, both for the initial volume measurement with no pellets, and for the final volume measurement with the test sample in the apparatus.

CONCLUSIONS

1. The linear method of volume measurement is a quick and simple way to estimate the volume of a sample. It should not be used where a great deal of accuracy is desired. It gave the same relative order of free swelling as the OKG, mercury displacement and buoyancy in water methods, i.e., pellet 2 >pellet 1> pellet 3 but overall free swelling values were much larger than for the other methods.
2. The buoyancy in water and OKG methods are both accurate methods of volume measurement. Both gave similar results in terms of pellet swelling and degree of reduction. However the reoxidation of reduced pellets by the buoyancy in water method makes it undersirable if any further analysis is desired.
3. The mercury displacement method gave the lowest free swelling values. Although this is the standard method, it is considered less reliable than the buoyancy method because of the intrusion of mercury into the pores of reduced pellets.
4. The relative free swelling of the pellets had an inverse relationship with the surface area and total pore volume of the pellets before reduction.
5. Free swelling during reduction was highest for pellets having the lowest amount of mesopore and macropore volumes.

Table 1 - Volume of samples before and after reduction measured by buoyancy in water, linear, and mercury displacement methods

Sample no.	Before reduction: Linear (cc)	Buoyancy in water (cc)	Mercury displacement (cc)	Lin/Hg (cc/cc)	H2O/Hg (cc/cc)	After reduction: Linear in water (cc)	Buoyancy displacement (cc)	Mercury (cc)	Lin/Hg (cc/cc)	H2O/Hg (cc/cc)	ΔV Linear %	ΔV H2O %	ΔV Hg %	Rf degree of reduction %
G1-1	12.1	12.1	12.1	1.00	1.01	15.2	14.2	13.2	1.15	1.08	20.4	14.1	8.3	48.6
	*σ=.224	*σ=.079	*σ=.079			*σ=.36	*σ=.099	*σ=.058						
G1-2	12.5	12.3	12.4	1.01	0.992	15.1	14.5	13.8	1.09	1.05	17.1	15.2	10.1	46.7
G1-3	13.2	13.3	13.3	0.992	1.00	-	15.5	14.7	-	1.05	-	14.2	9.5	-
G1-4	13.6	13.4	13.6	1.00	0.985	16.9	15.9	15.0	1.13	1.06	19.5	14.8	9.3	49.6
											χ=19.0	14.8	9.3	48.3
G2-1	11.9	11.9	11.9	1.00	1.00	15.5	14.1	13.3	1.17	1.06	23.2	15.6	11.8	44.4
	*σ=.297	*σ=.051	*σ=.090			*σ=.361	*σ=.156	*σ=.062						
G2-2	12.8	12.5	12.5	1.02	1.00	-	14.8	14.2	--	1.04	--	15.5	13.6	42.4
G2-3	12.3	13.3	13.4	0.918	0.993	16.6	15.8	14.9	1.11	1.06	25.9	15.8	11.2	45.1
G2-4	13.1	13.7	13.8	0.992	.985	17.2	15.7	14.9	1.15	1.05	23.8	17.2	12.9	44.8
											χ=24.3	16.0	12.4	44.2
G3-1	15.0	15.6	15.3	0.980	1.01	1.68	17.3	17.0	0.988	1.02	10.7	9.8	10.0	43.2
	*σ=.028	*σ=.076	*σ=.114			*σ=.52	*σ=.052	*σ=.078						
G3-2	14.7	14.9	15.1	0.974	k0.988	17.3	16.5	16.2	1.07	1.02	15.0	9.7	6.8	43.7
G3-3	13.6	13.9	14.0	0.971	0.993	14.8	15.5	15.3	0.967	1.01	8.1	10.3	8.5	42.6
G3-4	13.3	13.7	13.8	0.964	0.993	14.0	15.3	14.8	0.946	1.03	5.0	10.5	6.8	41.4
											χ=9.7	10.1	8.0	42.7
				χ=.985	χ=.997				χ=1.08	χ=1.04				
				σ=.027	σ=.010				σ=.082	σ=.021				

* Standard deviation for 10 repeated volumetric analyses on the first sample of each set

Table 2 Volume measurements, before and after reduction using the OKG and mercury displacement methods; per cent swellings (ΔV); and degree of reduction of three types of iron oxide pellets.

	Before reduction			After reduction					
Sample No.	OKG (cc)	(mercury displacement (cc)	OKG/Hg (cc/cc)	O.K.G (cc)	mercury displacement (cc)	OKG/Hg (cc/cc)	ΔV OKG %	ΔV mercury displacement %	Rf degree of reduction %
61-5	13.4	13.1	1.02	15.9	14.5	1.10	15.7	9.7	48.7
	*σ=0.075	*σ=0.075		*σ=0.138	*σ=0.067				
61-6	13.8	13.8	1.00	16.3	14.9	1.09	15.3	7.4	51.2
61-7	12.4	12.3	1.01	14.4	13.6	1.06	13.9	9.6	45.7
61-8	12.0	12.0	1.00	14.6	13.8	1.06	17.8	13.0	47.3
							X=15.7	X=9.9	X=48.2
62-5	14.2	14.2	1.00	16.9	15.2	1.11	16.0	6.6	40.4
	*σ=0.074	*σ=0.049		*σ=0.315	*σ=0.100				
62-6	13.2	12.9	1.02	16.0	14.8	1.08	17.5	12.8	42.9
62-7	12.3	12.1	1.02	14.8	13.5	1.10	16.9	10.4	45.5
62-8	13.0	12.5	1.04	15.7	15.0	1.05	17.2	16.7	46.5
							X=16.9	X=13.3	X=43.8
63-5	13.3	13.5	0.985	14.7	14.7	1.00	9.5	8.2	40.9
	*σ=0.052	*σ=0.100		*σ=0.090	*σ=0.045				
63-6	15.6	15.3	1.02	17.2	17.0	1.01	9.3	10.0	43.5
63-7	12.9	12.7	1.02	14.2	14.0	1.01	9.2	9.3	41.7
63-8	15.4	15.3	1.01	17.0	16.6	1.02	9.4	7.8	42.2
							X=9.4	X=8.8	X=42.1
			X=1.01			X=1.06			
			σ=.014			σ=.04			

Table 3 Porosity and surface area of pellets before and after reduction.

Sample No.	Open pores volume %	Macro/mesopores volume %	Micropores volume %	Surface area (m2/g)
G 1 BR	23.3	15.6	84.4	0.0965
G 1 AR(1-4)	49.0	50.8	49.2	0.416
G 1 AR(5-8)	51.2	58.4	41.6	0.401
G 2 BR	22.8	3.15	96.8	0.0928
G 2 AR(1-4)	49.7	44.9	55.1	0.340
G 2 AR(5-8)	48.5	68.8	31.2	0.273
G 3 BR	33.1	43.7	56.3	0.226
G 3 AR(1-4)	45.2	37.4	62.6	0.440
G 3 AR(5-8)	48.4	44.6	55.4	0.777

BR=before reduction; AR= after reduction; samples 1-4 were measured by the buoyancy in water, linear, and mercury displacement methods; samples 5-8 were measured by the OKG and mercury displacement methods.